

Optically-selective window coatings of precious metal nanoparticles

by

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Certificate of Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Abbreviations

AFM = Atomic Force Microscopy

APTS = aminopropyltrimethoxysilane

AR = aspect ratio

ATO = antimony tin oxide

BSE = Back Scattered Electrons

CTAB = hexadecyltrimethylammonium bromide

DDA = Discrete Dipole Approximation

DDSCAT = Discrete Dipole Approximation for Scattering and Absorption of Light by Irregular Particles

DPN = Dip Pen Nanolithography

e-beam = electron beam

EBL = Electron Beam Lithography

EBPVD = Electron Beam Physical Vapour Deposition

ENFOL = Evanescent Near Field Optical Lithography

EUV-IL = Extreme Ultraviolet – Interference Lithography

FIB = Focused Ion Beam

FSS = Frequency Selective Surface

FTO = fluorine tin oxide

HD = high density

HV = high vacuum

IBL = Ion Beam Lithography

IgG = anti-mouse immunoglobulin G

IPA = isopropyl alcohol

IPL = Ion Projection Lithography

ISO = International Organisation for Standardisation

ITO = indium tin oxide

p-beam = proton beam

PDMS = poly(dimethylsiloxane)

PLL = Planar Lens Lithography

PMMA = poly(methyl methacrylate)

PSS = poly(sodium styrenesulfate)

LBL = Layer by layer

LD = low density

MHA = mercaptohexadecanoic acid

MIBK = methyl isobutyl ketone

MicroSpec = SEE 2100 Microspectrophotometer

MPA = 3-mercaptoproponic acid

MPTS = 3-mercaptopropyltrimethoxysilane

MUA = 11-mercaptoundecanoic acid

NIL = Nanoimprint Lithography

NIR = near infrared

Nu_L = Nusselt Number

PE = Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer

Pr = Prandtl Number

PVA = poly vinyl alcohol

PVD = Physical Vapour Deposition

Re_L = Reynolds Number

RIE = Reactive Ion Etching

SAM = self-assembled monolayer

SC = Shading Coefficient

SE = Secondary Electrons

SEIRAS = Surface Enhanced Infrared Reflection Absorption Spectroscopy

SEM = Scanning Electron Microscopy

SERS = Surface Enhanced Raman Scattering

SFIL = Step and Flash Imprint Lithography

SHGC, F_{sol} = Solar Heat Gain Coefficient

SLG = soda lime glass

SPL = Scanned Probe Lithography

STM = Scanning Tunnelling Microscopy

T_{sol} = solar transmittance

T_{vis} , T_{lum} = visible transmittance

TCAB = tetradodecylammonium bromide

TCO = transparent conducting oxide

TMS = bis(ω -trimethylsiloxyundecyl)disulfide

T-NIL = Thermoplastic Nanoimprint Lithography

VP = Variable Pressure

VPSED = Variable Pressure Secondary Electron Detector

ZPAL = Zone Plate Array Lithography

Publications arising from this work

Journal Articles

N. Stokes, A. McDonagh, M. Cortie, 2007, 'Preparation of gold nanostructures by nanolithography', *Gold Bulletin*, **40**, 310.

M. Cortie, N. Stokes, A. McDonagh, 2009, 'Plasmon resonance and electric field amplification of crossed gold nanorods' *Photonics and Nanostructures – Fundamentals and Applications*, **7**, 143.

N. Stokes, J. Edgar, A. McDonagh, M. Cortie, 'Spectrally-selective coatings of gold nanorods on architectural glass' accepted 23rd January 2010, *Journal of Nanoparticle Research*, in press.

Conference Presentations

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Abstract

Energy-efficient window coatings limit the transfer of energy from one side of a window to the other. Their use has the potential to significantly reduce the electrical energy consumed by air conditioning, heating and lighting the interior space of a building. In particular, the use of spectrally selective coatings allows for more control over both the internal climate, the colour of the transmitted light, and the overall energy efficiency of the window coating. Gold nanoparticles, especially the optically anisotropic gold nanorods, offer a uniquely stable and long lasting solution to obtaining tuneable absorption of electromagnetic radiation for a wide range of potential applications. In this thesis the potential of gold nanorods as a spectrally selective coating for window glass is examined, the possible means of securing the nanorods to the glass are explored and their effectiveness as an optical coating compared to current commercially available coatings of similar design. The optical properties of these nanorods and some other shapes with potentially interesting properties are computationally modelled and are compared to the properties of samples fabricated using electron beam lithography and to samples made by wet chemistry. The work shows that gold nanostructures could serve as the basis for a new generation of spectrally-selective coatings for architectural glass.

Chapter 1 of this thesis reviews the fabrication, optical properties and potential applications of gold nanostructures. The fabrication methods reviewed include reported lithographic procedures as well as wet chemical techniques for the formation of gold nanostructures. The optical properties of the gold nanostructures are examined, and the phenomenon of surface plasmon resonance is analysed. Some potential applications for the optical properties of gold nanostructures are explored, and an appraisal is made of window glazing technologies including their operating mechanism. Also, the advantages of the various technologies are reviewed.

In Chapter 2, computational modelling of the optical properties of gold nanoparticles of rod, X and V shapes is carried out. The study shows the surface plasmon resonances of the gold nanoparticles are influenced by the dimensions, spacings and angles of the structures. The polarisation of the incoming light also affects the optical extinction

properties of the investigated nanoparticles. When the structures are aligned in a 1D array, the main surface plasmon resonance peaks are red-shifted compared to the isolated structure. An analysis of the electric field intensity as a function of distance from the structure is conducted to determine the potential use of these structures as an amplifier for two-photon fluorescence.

Chapter 3 explores the electron beam lithography fabrication process, including an examination of the effects of different substrates, chamber pressure, deposition parameters, dose characteristics and post-exposure processes. Due to the reduction in exposure time for conducting glass over insulating glass, further experimentation is conducted with a transparent conducting glass substrate. The formation of large arrays of high quality gold nanostructures is achieved through the comprehensive investigation of deposition conditions and in particular the addition of a short burst of plasma cleaning after the development step. Sufficient areas for rod and X arrays are fabricated to enable the measurement of the optical properties.

The optical properties of the electron beam lithographically fabricated structures are addressed in Chapter 4. A comparison is undertaken between the measured optical properties from structures produced in Chapter 3 to the modelled structures investigated in Chapter 2. Surface plasmon resonance peaks are found on each gold nanostructured sample investigated. However, the optical properties of a single layer of gold nanostructures are insufficient to produce an effective window coating.

Chapter 5 investigates the attachment of gold nanorods onto glass through an application of a molecular binding layer and immersion of the nanorods into a polymer. The use of 3-mercaptopropyltrimethoxysilane to bind gold to glass is found to increase the amount of gold nanorods attaching to glass compared to samples without the binding molecule. However, the immersion of gold nanorods into a polymer layer is found to have the most potential for use as a window coating, as careful control over the gold nanorod concentration could be used to adjust the required optical properties. Mixtures of different aspect ratio gold nanorods combine the different longitudinal plasmon resonances to absorb light over a larger spectral range. Control over the aspect ratio of the nanorods included in the film, ensured control over optical properties. The

optical transmission properties of the large area films of gold nanorod mixtures provided superior window transmission properties in the spectral range 700 – 900 nm compared to a currently commercially available solar laminate window coating.

In Chapter 6 the effect of an electric field on gold nanorods in solution is investigated. Prior reports suggested that the gold nanorods could be aligned under the influence of an AC electric field. No alignment was observed here for wet-chemically produced gold nanorods, with a CTAB stabiliser, when under the influence of an AC or DC electric field. A DC electric field of sufficient strength is found to strip the gold nanorods of the CTAB stabilising agent, which results in gold depositing on the positive electrode.

The final chapter of this thesis, Chapter 7, summarises the work presented and highlights the significant conclusions. It also outlines some directions for possible further research built on and extending from the work presented here.